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# Thermochemistry and Kinetics of the Reactions of Apatite Phosphates with Acid Solutions (II)

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Additional information is available at the end of the chapter

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## Abstract

The principal material in the phosphate ores is composed of calcium fluorapatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , in which the various components have been partially substituted by magnesium, sodium, carbonate, and hydroxyl ions. These substitutions affect the stability of the material and its reactivity toward the acid attack. The present chapter reports the influence of carbonates and magnesium on these properties. Using different calorimeters, dissolution experiments of carbonated and noncarbonated Ca and Ca/Mg apatites were carried out in acid solutions leading to thermochemical quantities. The results show that substitution of carbonate for F ions in the channel (to get A-type carbonate F-apatites) results in increasing the stability of the edifice, while substitution of  $\text{CO}_3$  for  $\text{PO}_4$  in fluor- or hydroxyapatites (to get B-type apatites) leads to a decrease in stability. The latter phenomenon was also observed when substituting magnesium for calcium in F-apatites. The presence of the former in the apatite structure results in an increase of the speed of dissolution in acid solution that is enhanced when carbonate is also replacing phosphate groups. Dissolution mechanism of synthesized Ca/Mg F-apatites seems to be a one-step process, while dissolution of a Gafsa (TN) natural phosphate to get superphosphate fertilizer is more complex.

**Keywords:** carbonate apatites, enthalpy of formation, Gibbs free energy, acid attack, phosphate ore, kinetic models

## 1. Introduction

The “wet” manufacturing process of phosphoric acid is based on the attack of natural phosphates by nitric, hydrochloric, or sulfuric acid or the mixture of the latter with diluted phosphoric acid solution. Super phosphate fertilizers are produced industrially through the reaction of phosphoric acid with natural phosphates.

According to Pierre Becker [1], “the most important (mineral) for the phosphoric acid industry is the apatite group:  $(\text{Ca}, \text{Na}_2, \text{Mg})_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x\text{F}_y(\text{F}, \text{OH})_{2-y}$ ” This formula is representative of a large variety of compounds in which the compositions in the major constituents, that is, calcium, phosphorus, and fluorine, lie in the ranges 29.3–53.6, 23.8–40.3, and 1.3–4.1 w% CaO,  $\text{P}_2\text{O}_5$  and F, respectively (P. Becker). The deposit compounds are probably the most stable ones appearing in their respective geological conditions of temperature, pressure, and composition in different elements.

It would be interesting to apprehend the contribution of each component in the stability and reactivity of the natural products. However, as it is impossible to reproduce the formation conditions of the latter, one can proceed by a progressive approach which consists in determining these properties for synthetic limit products then for their “derivative” which can be obtained by introduction of various elements or entities in the former. Thermodynamics allows to quantify the stability of the compounds through the determination of their Gibbs free energy of formation and gives a comparison between compounds having molar weights in the same order of magnitude. Kinetic studies of the acid attack allow to characterize the reactivity of the compounds in terms of rapidity, to propose an attack mechanism and highlight the influence of some parameters on the reaction rate.

Because of the predominance in the ore of the components cited above, Ca-fluorapatite (Ca-FAP),  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , has been considered as the more representative compound of natural phosphates and has been widely studied under various aspects. This is also because of the similarity of their crystal structures. Ca-hydroxyapatite (Ca-HAP),  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , comes in the second position and constitutes the model compound in studying the properties of the mineral component of calcified tissues (enamel, dentine, and bones).

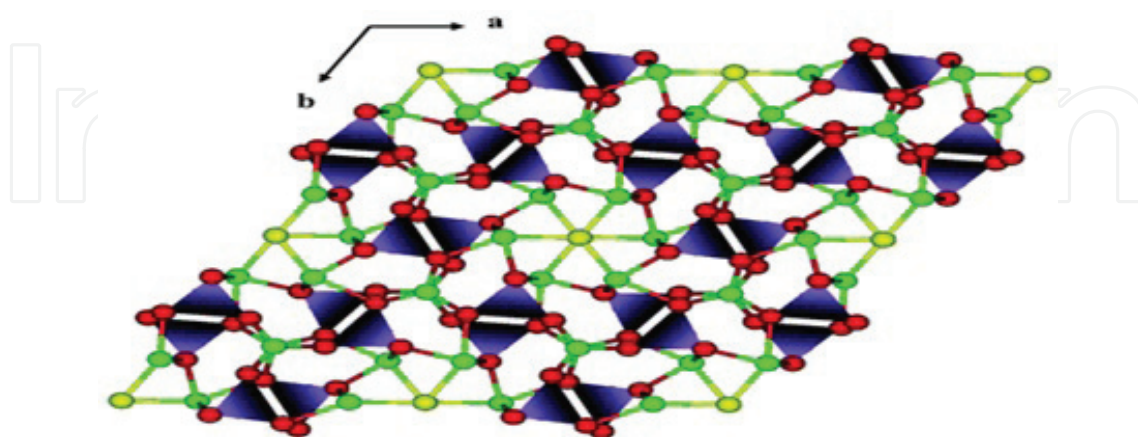
Ca-FAP seems to be crystallographically characterized for the first time by Leonhardt in 1923 (cited in ref. [2]). The structure has been confirmed in 1930 [2, 3]. Since then a wide varieties of works have been performed [4], but the first chapter related to thermochemistry of this compound has been published by Gottschall in 1958 [5] who dissolved Ca-FAP in nitric acid and determined its formation enthalpy. At the end of the 1990s, a lot of thermochemistry works started on Ca-FAP and analogous compounds containing Ba, Sr, Mg, Cd, and Pb, in order to determine their dissolution energies and to deduce their formation enthalpies. In absence of formation entropies, these results allowed to compare the stability of the compounds based on the formation enthalpies and not on the Gibbs free energies, as required. Then the entropy factor has been estimated by a calculation procedure combining literature data [6]. This allowed to propose a more realistic scale of stability of these compounds. The same calculation procedure has been applied for hydroxy and chlor-apatites containing the metal reported above. All these results are gathered in reference [7]. Substitutions of calcium by alkali earth metals, Cd or Pb have also been considered thermochemically and have been widely published in literature. In the phosphate ore, these substitutions are minor in comparison to carbonate substitutions. This chapter deals with the stability and reactivity of some carbonate apatites and reports thermodynamic and kinetic studies of the attack of a sample ore from Gafsa (Tunisia) by phosphoric solution having different composition.

## 2. Carbonate substitutions in the apatites

The model compound, Ca-FAP, crystallizes in the hexagonal system with space group  $P6_3/m$ . The structure has been refined from diffractometer single-crystal X-ray data in 1972 [4]. The corners of the hexagonal unit cell are occupied by calcium ions, called Ca(1), which are also present at the center of the  $c$ -axis parameter. These columns of  $\text{Ca}^{2+}$  ions are linked together by  $\text{PO}_4$  tetrahedron groups that are positioned along both sides of the hexagonal faces. The other six calcium, called Ca(2), form two triangles rotated by  $60^\circ$  from each other around the  $c$ -axis and are located at  $\frac{1}{4}$  and  $\frac{3}{4}$  positions along this axis, forming a channel. In FAP, the center of each triangle is occupied by a F ion, while in hydroxy and chlorapatites, hydroxyl, and chloride ions are above this position. **Figure 1** shows the projection of the FAP lattice on the  $a$ ,  $b$  plane.

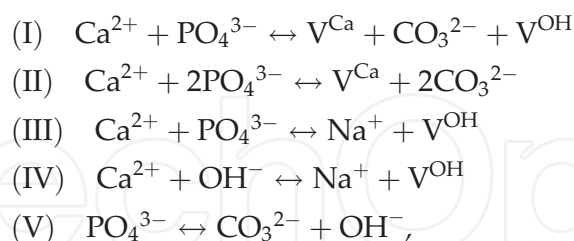
Carbonate can substitute for F (or OH) along the channel or for  $\text{PO}_4$  groups, leading to “A” or “B” type carbonate apatites, respectively. A-type carbonate apatites are synthesized by solid gas/reaction at high temperature while the B-type ones are precipitated in aqueous solution. AB-type carbonate apatites have either been prepared by solid/gas reaction performed on rich carbonate B-type ones [4], or by precipitation in conditions similar to that used for the synthesis of Ca-deficient hydroxyapatites [8]. Each type of compounds are characterized crystallographically by specific displacements of some rays on the X-ray profiles and spectroscopically by the appearance of special bands on the IR recordings. They also differ in some properties among them, the thermodynamic ones, as seen below.

Fluoride (or hydroxyl) replacement mechanism leading to A-type carbonate apatites is commonly supposed to be accompanied by the appearance of an anion vacancy along the channel. This seems to be accepted without any ambiguity while in the B-type ones, substitution of  $\text{PO}_4$  by  $\text{CO}_3$  has been subjected to a large number of suggestions resulting from various methods of treatment of the analytical results.



**Figure 1.** Projection on  $a,b$  plane of the Ca-FAP structure showing Ca(1) in green, O in red,  $\text{PO}_4$  in blue, and F in yellow at the center of Ca(1) hexagons. Ca(2) are not represented .

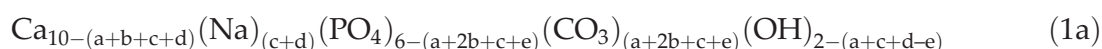
In 1993, De Mayer and Verbeeck [9] gathered the various substitution mechanisms that can be considered in B-type carbonate hydroxyapatites containing sodium. These mechanisms are as follows:



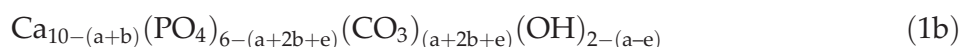
where  $\text{V}^{\text{Ca}}$  and  $\text{V}^{\text{OH}}$  stand for vacancies of  $\text{Ca}^{2+}$  and  $\text{OH}^-$

Replacement mechanisms I– IV are accompanied by creation of a vacancy in the Ca or OH site, while in mechanism V,  $\text{PO}_4$  is replaced by the tandem  $(\text{CO}_3\text{OH})$ . The latter mechanism has been suggested considering the analogy with the fluoride analogous apatites in which the chemical analysis reveals the presence of more fluoride than in free carbonate fluorapatite.

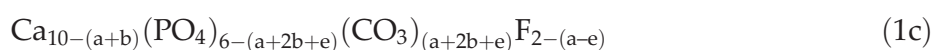
Suppose  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  are the respective contributions of these mechanisms, the general formula of the apatite will be:



In Na free B-type hydroxyapatites, only mechanisms I, II, and V have to be considered. So “ $c$ ” and “ $d$ ” factors should be nil and the general formula is derived as:



For the fluoride homologous compounds the formula becomes as:



This formula is equivalent to that proposed in 1963 by Köhl and Nebergall who “appear to have been the first to propose the formula:  $\text{Ca}_{10-x+y}(\text{PO}_4)_{6-x}(\text{CO}_3)_x\text{F}_{2-x+2y}$ ” [10] with  $x = a + 2b + e$  and  $y = b + e$ . Formula (1c) supposes that among the “ $a + 2b + e$ ” carbonates introduced in fluorapatite “ $e$ ” are associated to F as  $(\text{CO}_3\text{F})$  entities and the remaining “ $a + 2b$ ” are accompanied by the creation of “ $a + b$ ” vacancies in the Ca sites.

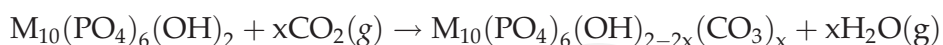
### 3. Thermochemistry of some A-type carbonate apatites

Thermochemistry dissolution of A- and B-type carbonate apatites has been undertaken in the beginning considering experiments performed with low values of the solid/liquid ratio. This led to a simple dissolution without the appearance of any precipitate. As reported, the latter appears with higher values of this ratio.



### 3.1. Enthalpies of dissolution in nitric acid solution

Calcium, strontium, and barium A-type carbonate hydroxyapatites have been prepared by solid/gas carbonation of the corresponding hydroxyapatites, according to the general reaction scheme:



where M stands for calcium, strontium, or barium.

The starting solids were heated in pure CO<sub>2</sub> flowing gas at temperature between 700 and 1000°C during half an hour to 6 days. By varying the temperature and time they were progressively carbonated until full substitution of hydroxyl ions leading to pure A-carbonate apatites. The synthesized products were characterized by X-ray and IR analyses. All of them showed the IR bands characterizing such kinds of apatites and exhibit a nonmonotonous slight variation of “c” parameter, while “a” parameter and lattice volume increase appreciably over the carbonate content. The carbonate amount was determined by C-H-N analysis (for Ca-bearing compounds [11]), coulometry, and Rietveld processing (for Sr compounds [12]) or thermogravimetrically (for Ba compounds [13])

The solids were then dissolved in a 3 or 9 wt% nitric acid solution using a home-made isoperibol calorimeter. The device was previously described in detail [14]. Carbon dioxide gas was continuously bubbled in the liquid phase to avoid its retention after dissolution of carbonated products. The heat effect produced in the calorimetric cell was manifested by the variation of the temperature of the reaction medium which was detected by a thermistance probe acting as one of the four arms of a Wheatstone bridge. The balance voltage was amplified by a Keithley multimeter and then recorded over time. The solid to be dissolved or the liquid to be diluted was carefully introduced in a thin-walled glass bulb that was manufactured at one of the extremities of a Pyrex tube (5 mm diameter). Experiment started by searching a quasi-steady state in which the electrical current was practically null and the baseline deviated slightly from the vertical line. The reaction was started by breaking the bulb using a thin glass baton and the heat effect dissipated in the medium results in a deviation of the signal, which then became parallel to the previous baseline. The shift between the baselines is proportional to the corresponding heat effect. More details on the calibration and heat effect determination are exposed in Ref. [12]. Experimental results processing and errors calculation are developed in Ref. [13].

**Figures 2–4** show the variation of the molar energies of solution for Ca, Sr, and Ba compounds as functions of the amount of carbonate in the lattice.

Depending on the cation, the enthalpy of solution decreases (Sr in 9 wt% HNO<sub>3</sub>), increases (Ba in 3% HNO<sub>3</sub>), or shows a bell-shaped curve (Ca in 9 wt% HNO<sub>3</sub>).

### 3.2. Formation enthalpies of A-type carbonate apatites

The solution enthalpy of a particular compound can be involved in a hypothetical reaction containing other compounds for which the enthalpies of formation are previously tabulated.

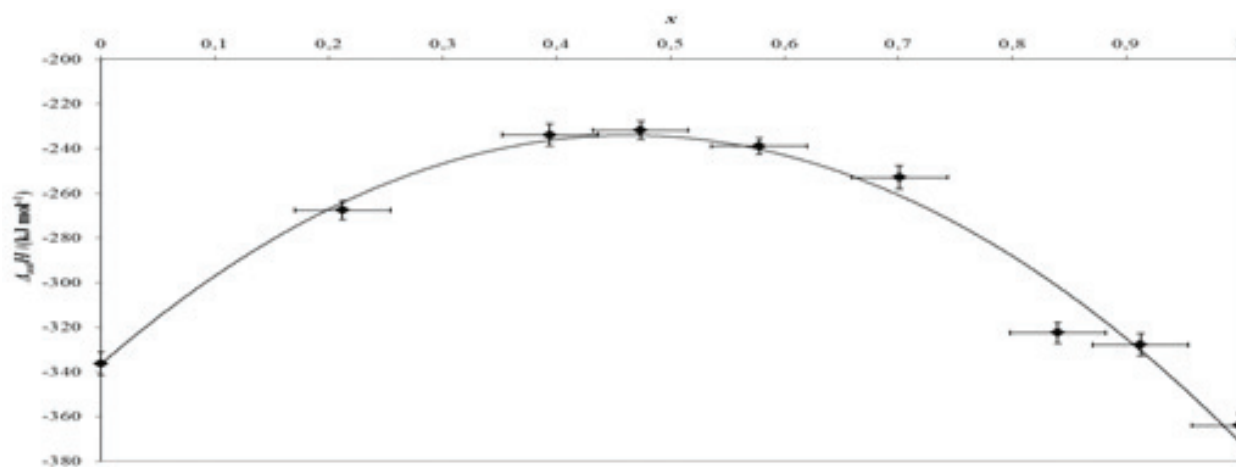


Figure 2. Standard molar enthalpy of solution at 298 K in 9 wt% nitric acid solution for  $\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)_x(\text{OH})_{2-2x}$  over  $x$  [11].

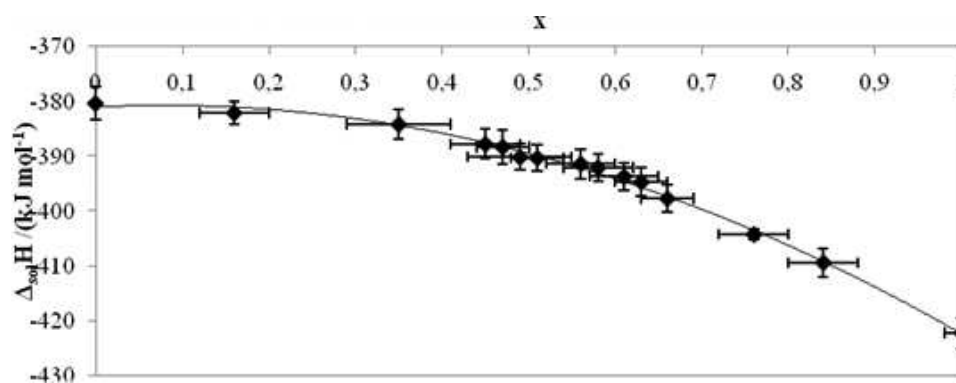


Figure 3. Standard molar enthalpy of solution at 298 K in 9 wt% nitric acid solution for  $\text{Sr}_{10}(\text{PO}_4)_6(\text{CO}_3)_x(\text{OH})_{2-2x}$  over  $x$  [12].

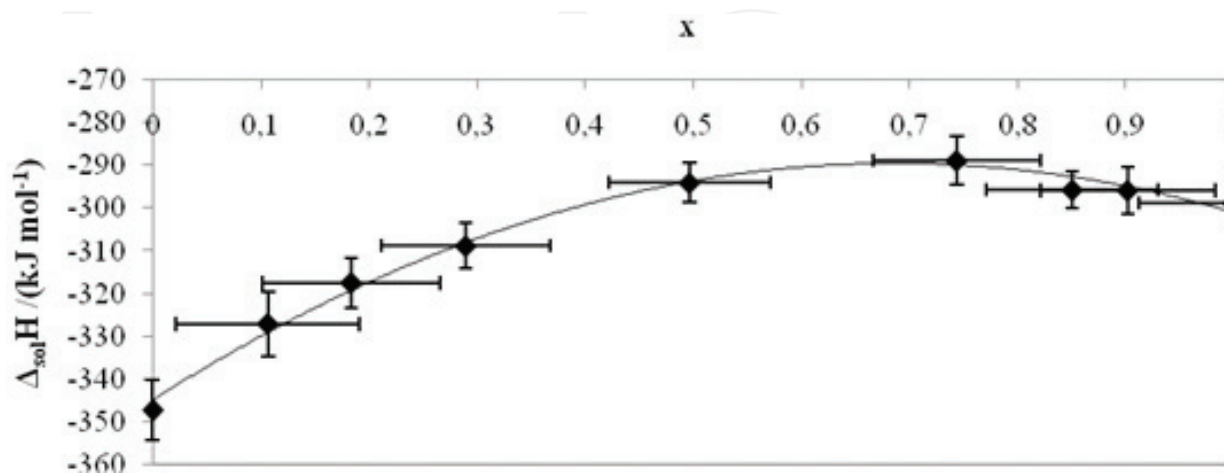
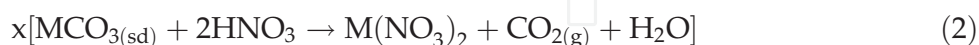
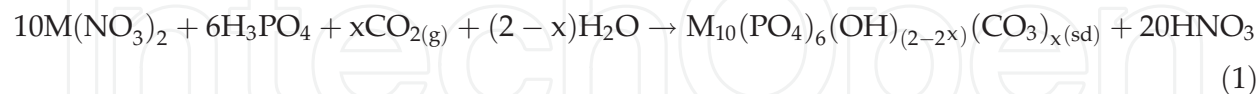


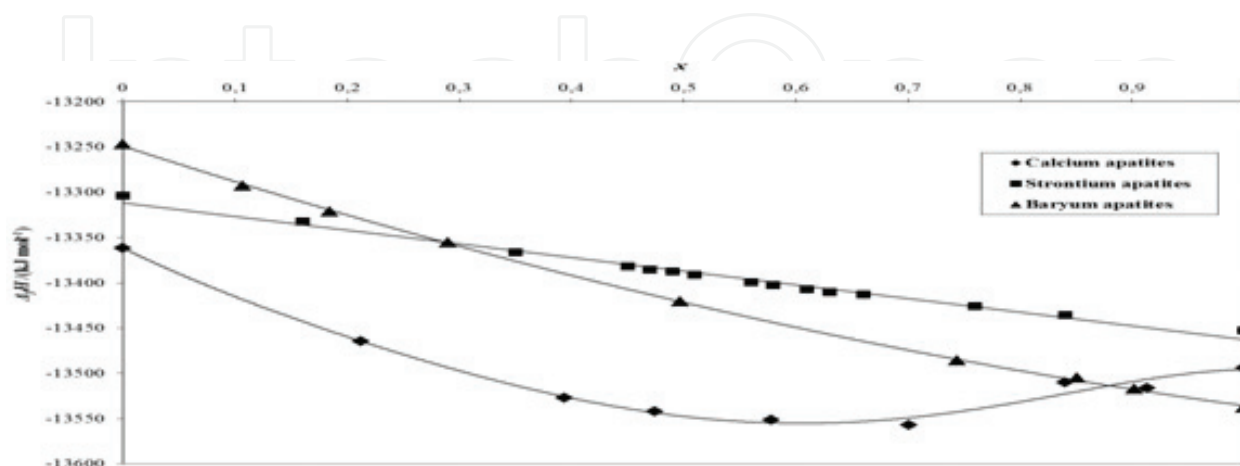
Figure 4. Standard molar enthalpy of solution at 298 K in 3 wt% nitric acid solution for  $\text{Ba}_{10}(\text{PO}_4)_6(\text{CO}_3)_x(\text{OH})_{2-2x}$  over  $x$  [13].

The difference between the enthalpies of solution of the compounds in both sides of that reaction leads to the formation enthalpy of the product in concern. Example,  $M_{10}(PO_4)_6(OH)_{2-2x}(CO_3)_x$  can be involved in a reaction containing  $MCO_{3(sd)}$ ,  $M(OH)_{2(sd)}$ , and  $M_3(PO_4)_{2(sd)}$ .

The dissolution reactions or their reverse are schematized as follows. Their “sum” leads to the final reaction.



In addition to the dissolution reaction of the apatite (Step 1), this scheme includes the dissolution of  $x$  moles of M-carbonate (Step 2),  $(1-x)$  moles of M-hydroxide (Step 3), and 3 moles of trimetallic phosphate (Step 4). Their corresponding enthalpies were measured in the same solvent under similar conditions as for the apatites. The results are reported in Ref. [11] for calcium, [12] for strontium, and [13] for barium, together with the formation of enthalpies of the corresponding reactants. The latter were picked from the literature. **Figure 5** gathers the standard formation enthalpies over  $x$  for the three alkali earth metals. One can notice a monotonic variation for Sr and Ba compounds and a minimum at about  $x = 0.6-0.7$  for Ca ones. Sr carbonate apatites seem to be less stable than the others.

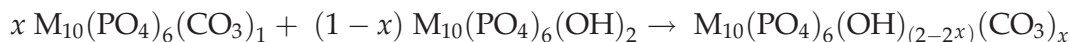


**Figure 5.** Comparative results of the standard formation enthalpy at temperature  $T = 298.15$  K and pressure  $p = 0.1$  MPa of carbonate hydroxyapatites  $M_{10}(PO_4)_6(OH)_{(2-2x)}(CO_3)_x$ , where  $M = Ca, Sr, \text{ and } Ba$  [11].



### 3.3. Enthalpy of mixing in the solid state

$M_{10}(PO_4)_6(OH)_{(2-2x)}(CO_3)_x$  can be considered as a solid solution obtained by mixing  $M_{10}(PO_4)_6CO_3$ <sub>(sd)</sub> and  $M_{10}(PO_4)_6(OH)_2$ <sub>(sd)</sub> according to the following scheme:



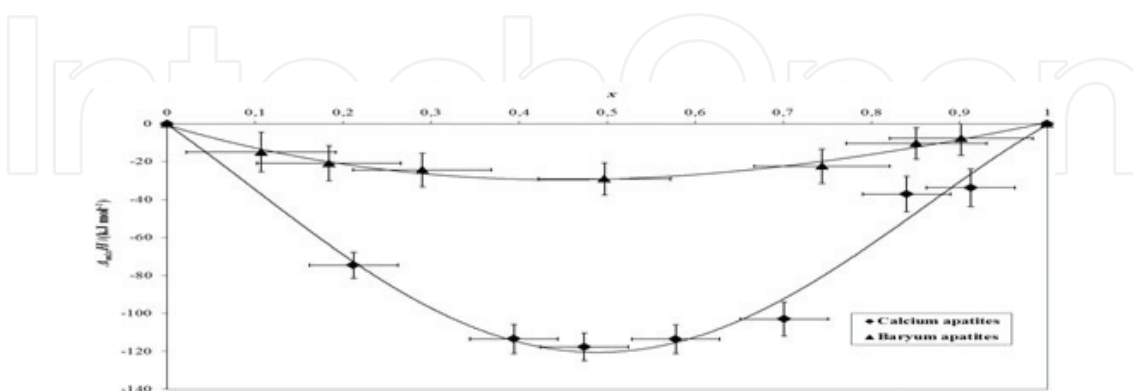
The molar enthalpy of mixing can be determined from the solution enthalpies of the reactants and product as follows:

$$\Delta_{\text{mix}}H^\circ(x)/(kJ\text{mol}^{-1}) = -\Delta_{\text{sol}}H^\circ(x) + x\Delta_{\text{sol}}H^\circ(x=1) + (1-x)\Delta_{\text{sol}}H^\circ(x=0)$$

This quantity can also be deduced from **Figure 5** by considering the difference between the enthalpy of formation of the solid solution for a given composition and that deduced from the straight line joining the points corresponding to the limit products. The latter quantity equals the enthalpy of formation of the heterogeneous mixture of the limit products. **Figure 6** shows the results for calcium and barium compounds. For strontium, **Figure 5** shows a linear variation over “ $x$ ” and so the mixing enthalpy is null in the all composition range, indicating that for that element, the solid solution of the limit products is an athermal one. This means that the energy bonds between the entities in the carbonate product are of the same order of magnitude as their corresponding ones in the hydroxyl compound.

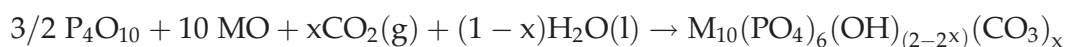
### 3.4. Estimation of the Gibbs free energy of the A-carbonate apatites

The stability of compounds having similar chemical formulae can be estimated considering in a first approximation numerical values of their formation enthalpies. The lower the value, the more stable is the corresponding compound. This way of doing supposes the formation entropy as zero. This quantity is negative and this assumption supposes zero as the upper limit of  $\Delta_f S^\circ$ . However, it is possible to seek a negative upper limit and set up a more realistic stability scale, taking into account the literature data. This is done as follows.



**Figure 6.** Variation of the mixing enthalpy of the solid solution *versus* “ $x$ ” at temperature  $T = 298.15$  K and pressure  $p = 0.1$  MPa for calcium and barium type A  $CO_3$ -apatites.

Carbonate apatite having the general formula  $M_{10}(PO_4)_6(OH)_{(2-2x)}(CO_3)_x$  can be obtained according the following reaction:



The standard entropy of this reaction at  $T^\circ$  (298K),  $\Delta_r S^\circ$ , can be expressed as a function of the standard entropies at  $T^\circ$  of the reactants and product as:

$$\Delta_r S^\circ = S^\circ(CO_3Ap) - 3/2 S^\circ(P_4O_{10}) - 10.S^\circ(MO) - x.S^\circ(CO_2) - (1 - x).S^\circ(H_2O)$$

Because of the increase in disorder accompanying this reaction, its entropy should be negative and so

$$S^\circ(CO_3Ap) < 3/2 S^\circ(P_4O_{10}) + 10.S^\circ(MO) + x.S^\circ(CO_2) + (1 - x).S^\circ(H_2O).$$

The absolute entropy of the CO<sub>3</sub>-apatite can be derived from the entropy of its formation,  $\Delta_f S^\circ(CO_3Ap)$ , and the absolute entropies of the elements (M, P, C, O<sub>2</sub>, and H<sub>2</sub>) in their most stable states as:

$$S^\circ(CO_3Ap) = \Delta_f S^\circ(CO_3Ap) + 10.S^\circ(M) + 6.S^\circ(P) + x.S^\circ(C) + (13 - x/2).S^\circ(O_2) + (1 - x).S^\circ(H_2)$$

Taking into account the inequality above, one can derive the following relationship:

$$\begin{aligned} \Delta_r S^\circ(CO_3Ap) &< 3/2 S^\circ(P_4O_{10}) - 6.S^\circ(P) + 10.[S^\circ(MO) - S^\circ(M)] + x.[S^\circ(CO_2) - S^\circ(C)] \\ &+ (1 - x).[S^\circ(H_2O) - S^\circ(H_2)] - (13 - x/2).S^\circ(O_2) \end{aligned}$$

The second term of this inequality is negative and constitutes the upper limit value of the formation entropy, instead of zero. If one supposes  $\Delta_r S^\circ(CO_3Ap)$  as equal to this limit, one can calculate a more realistic value of the Gibbs free energy of formation.

Taking into account the literature data for  $P_4O_{10}$  [15] and for the other elements and compounds [16], this assumption led to the general formula for the formation entropy as:

$$\Delta_r S^\circ(CO_3Ap) = -2992.23 + 165.99.x + 10.[S^\circ(MO) - S^\circ(M)]$$

And so the standard formation entropy of the apatite is linear over the carbonate content ( $x$ ) with an intercept value depending on M (= Ca, Sr, or Ba).

These results have been associated with the formation enthalpies previously published to lead to the Gibbs free energies of formation of the Ca, Sr, and Ba A-carbonate apatites, **Table 1** and **Figure 7**.

This figure confirms the less stability of Sr compounds and the particular behavior of the Ca ones.

X in Ca ap.	$\Delta_f G^\circ$ (T°)	x in Sr ap.	$\Delta_f G^\circ$ (T°)	x in Ba ap.	$\Delta_f G^\circ$ (T°)
0	-12488.276	0	-12438.89	0	-12412.3
0.212	-12601.77	0.16	-12475.81	0.107	-12466.59
0.394	-12673.78	0.35	-12519.21	0.184	-12498.41
0.474	-12692.73	0.45	-12540.16	0.29	-12537.66
0.587	-12706.88	0.47	-12544.15	0.497	-12611.9
0.701	-12718.97	0.49	-12547.14	0.744	-12687.13
0.84	-12678.85	0.51	-12552.13	0.851	-12711.42
0.913	-12688.46	0.56	-12562.61	0.902	-12724.94
1	-12670.77	0.61	-12573.08	1	-12753.79
		0.63	-12577.07		
		0.66	-12581.56		
		0.76	-12598.51		
		0.84	-12612.47		
		1	-12637.38		

Table 1. Estimated free energies of formation of the A-carbonate apatites.

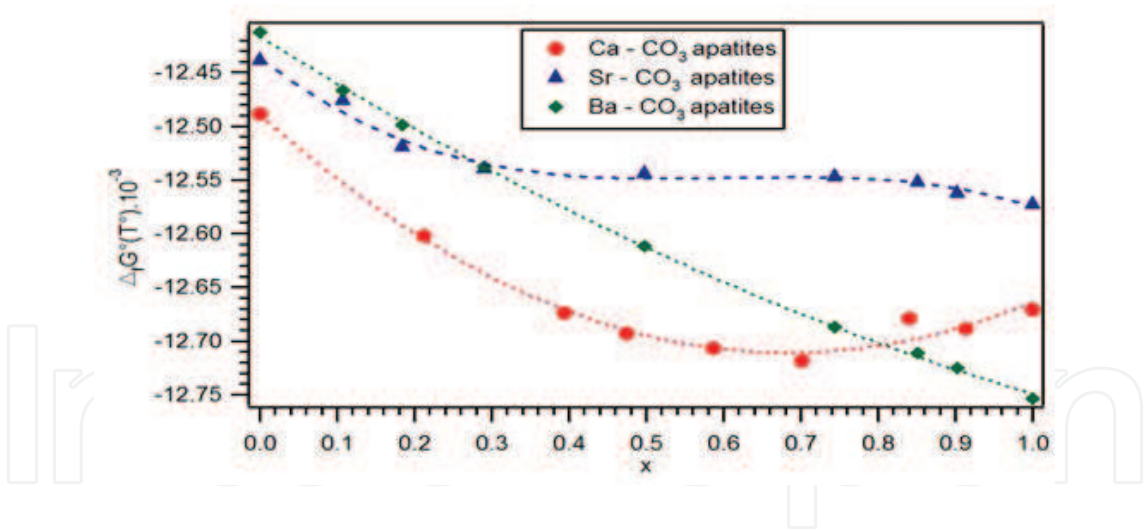


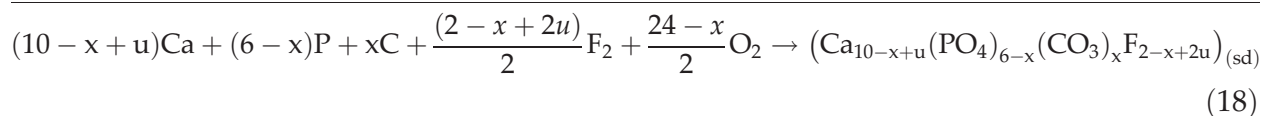
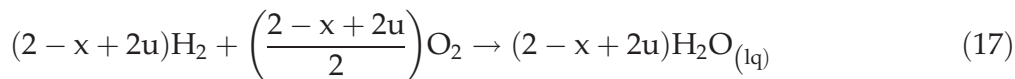
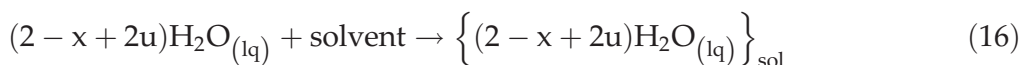
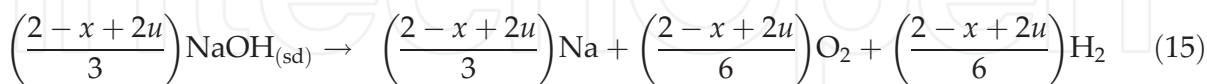
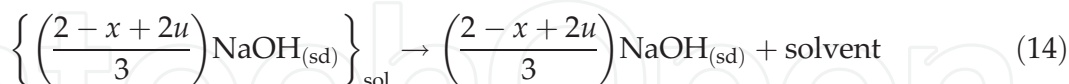
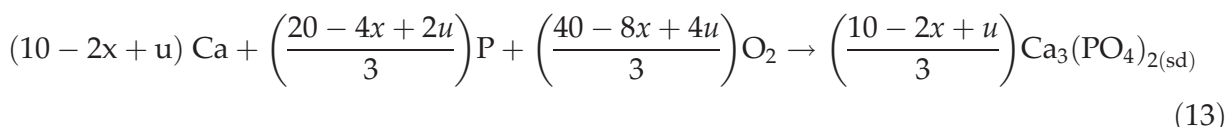
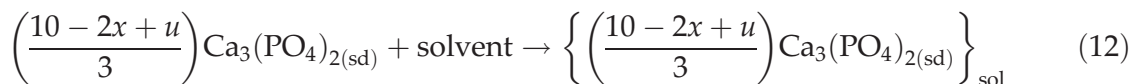
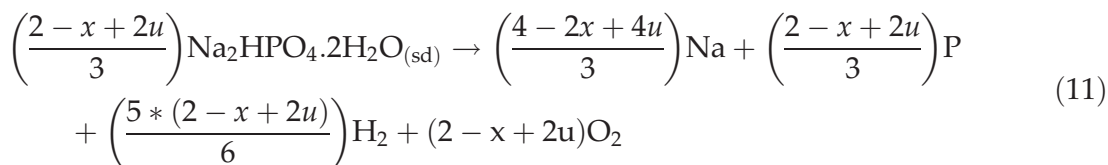
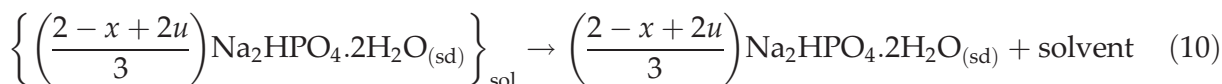
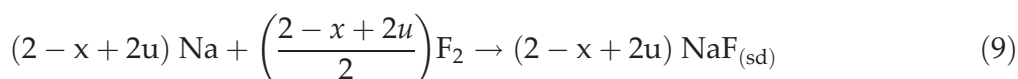
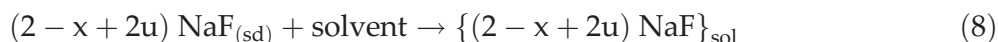
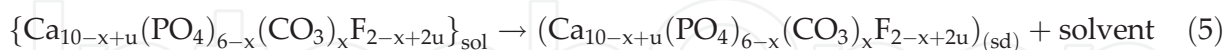
Figure 7. Variation of the standard Gibbs free energies of formation of the type A-carbonate F-apatites as functions of carbonate content 'x'.

## 4. Thermodynamics of some B-type carbonate Ca-fluorapatites

### 4.1. Formation enthalpy

Beside the procedure developed previously for determining the formation enthalpy of an apatite, this quantity can also be obtained from dissolving the apatite then other compounds whose dissolutions lead to the same entities in solution as that obtained with the apatite.

However, dissolution of the later introduces new entities in the thermochemical cycle. These entities are compensated by considering supplementary reactions involving dissolution or formation of well-known products. A typical case is illustrated by the cycle leading to the formation enthalpy of the apatite of formula:  $\text{Ca}_{10-x+u}(\text{PO}_4)_{6-x}(\text{CO}_3)_x\text{F}_{2-x+2u}$  ( $u$  instead of  $y$  in Section 2) [17]:

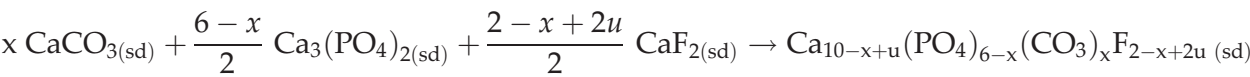


With  $0 \leq x \leq 2$  and  $u \leq x/2$  and the subscript “sol” means “in solution.”

This cycle gathers a succession of 13 steps whose “summation” leads to step 14 which represents the formation reaction of the apatite. Steps 1, 2, 4, 6, 8, 10, and 12 are dissolution reactions (or their reverse) of the carbonate apatite and well-known products. Their enthalpies were determined by performing experiments at 298 K in the same solvent (aqueous solution having 26.22 wt% H<sub>3</sub>PO<sub>4</sub>) using a SETARAM microcalorimeter. Steps 3, 5, 7, 9, 11, and 13 are formation reactions or their reverse. The corresponding enthalpies were picked from the literature.

4.2. Formation of Gibbs free energy

Calculation of the formation entropy has been undertaken according to the procedure developed above considering the negative entropy value of the following reaction between CaO, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, and CaF<sub>2</sub> as:



with  $0 \leq x \leq 2$  and  $u \leq x/2$ .

This led to derive the formation entropy of the carbonate apatite as a function of  $x$  and  $u$  and to determine the Gibbs free energy of formation for free carbonate FAP and four carbonate F-apatites having  $x$  in the range 0.27–1.22, **Table 2** [17]. One can notice an increase in the later quantity as the carbonate content increases. It seems that, in opposition of the A-type case, introduction of carbonate to form B-type carbonate apatites results in increasing the Gibbs energy and thus reducing the stability of the edifice.

Chemical formula	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$\Delta_f S^\circ / \text{J mol}^{-1} \text{ K}^{-1}$	$\Delta_f G^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{ K}^{-1}$
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	–	–	–13744	–
	–	–	–13548	–2423
	–	–	–13744	–
				–12979
				775.8
Ca <sub>9.88</sub> (PO <sub>4</sub> ) <sub>5.73</sub> (CO <sub>3</sub> ) <sub>0.27</sub> F <sub>2.03</sub>	–13511	–2514	–12762	770.3
Ca <sub>9.84</sub> (PO <sub>4</sub> ) <sub>5.49</sub> (CO <sub>3</sub> ) <sub>0.51</sub> F <sub>2.20</sub>	–13390	–2495	–12646	770.5
Ca <sub>9.65</sub> (PO <sub>4</sub> ) <sub>5.02</sub> (CO <sub>3</sub> ) <sub>0.98</sub> F <sub>2.27</sub>	–13033	–2438	–12306	760.2
Ca <sub>9.55</sub> (PO <sub>4</sub> ) <sub>4.78</sub> (CO <sub>3</sub> ) <sub>1.22</sub> F <sub>2.32</sub>	–12852	–2408	–12134	755.3

[a] = values from the literature.

**Table 2.** Standard molar enthalpies, entropies, and Gibbs free energies of formation of the “B” type carbonate fluorapatites at the temperature  $T = 298.15 \text{ K}$  and pressure  $p = 0.1 \text{ MPa}$  [17].

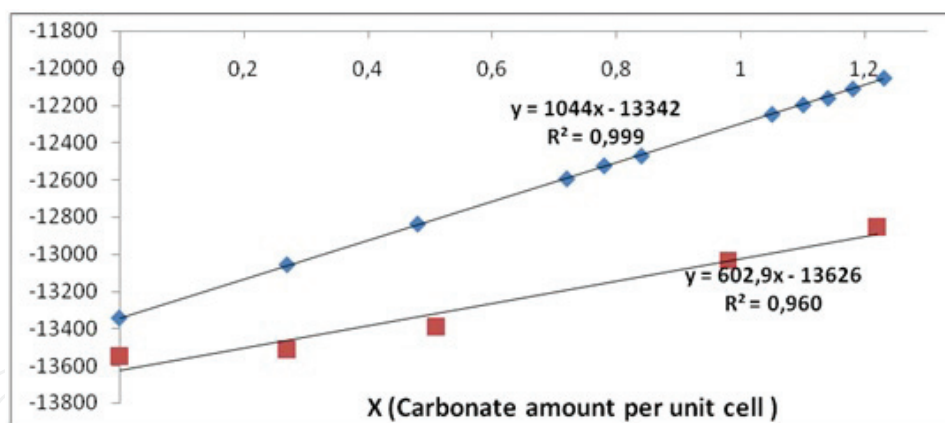
5. Thermochemistry of B-type carbonate Ca/Mg fluorapatites

In natural phosphates, calcium is weekly substituted by other cations, among them magnesium is the most important. Even existing in a few amounts, this element influences the thermochemical properties of the apatite and its reactivity toward the acid attack.

In contrast with other elements such as strontium, barium, lead, or cadmium, substitution of calcium by magnesium in fluor and hydroxyl-apatites does not exceed one atom per unit cell [18], while substitution by the other elements can lead to continuous solid solutions.

A series of B-type carbonate Ca/Mg fluorapatites containing various amounts of carbonate and  $0.90 \pm 0.01$  Mg atom per unit cell have been prepared, characterized, and chemically analyzed. They were then dissolved in a 3 wt% HCl solution [or HCL, 53.53 H<sub>2</sub>O] using the isoperibol calorimeter. During dissolution, the solution was saturated by a continuous bubbling of CO<sub>2</sub> gas. Many other complementary experiments were performed in the same device and solvent in order to get the formation enthalpies of the synthesized products. These processes concern dissolution of solids CaCl<sub>2</sub>, 2H<sub>2</sub>O, and MgCl<sub>2</sub> and dilution of [H<sub>3</sub>PO<sub>4</sub>, 0.756 H<sub>2</sub>O], [HF, 1.708 H<sub>2</sub>O]. The results were combined with the required formation enthalpies picked from the literature to give the formation enthalpies represented in **Figure 8** together with that corresponding to free magnesium carbonates. The curve corresponding to the latter was drawn from values reported in reference [17].

One can notice that the introduction of  $0.90 \pm 0.01$  Mg atom in the unit cell results in the increase of the formation enthalpy and so a decrease in stability. This is in agreement with the results reported by Drouet [19] in the compilation of thermodynamic quantities of a large number of apatites. Besides, the difference in stability depends on the carbonate content in the lattice, the higher the latter the less stable is the Mg-bearing apatite compared to its homologous Mg-free one.



**Figure 8.** Standard enthalpies of formation of B-type carbonate Ca and Ca/Mg fluorapatites (red color for Ca [17] and blue for Ca/Mg).

## 6. Thermochemistry of some B-type carbonate hydroxyapatites

B-carbonate Ca-hydroxyapatites have been synthesized, characterized, and chemically analyzed. They were then dissolved in a 9 wt% nitric acid solution (or H<sub>3</sub>PO<sub>4</sub>, 35.35 H<sub>2</sub>O) using the isoperibol calorimeter. The dissolution reaction of the compound having the general formula Ca<sub>10-(a+b)</sub>(PO<sub>4</sub>)<sub>6-(a+2b+e)</sub>(CO<sub>3</sub>)<sub>(a+2b+e)</sub>F<sub>2-(a-e)</sub> has been engaged in a succession of other reactions involving dissolution of Ca(NO<sub>3</sub>)<sub>2</sub>, 4H<sub>2</sub>O, dilution of H<sub>3</sub>PO<sub>4</sub>, 35.35 H<sub>2</sub>O, and formation of



well-known products and entities [20]. Each of these processes has been affected by a suitable factor so as the “summation” of the reaction succession led to the formation enthalpy of the apatite. The results allowed to derive the latter quantity as a function of the dissolution enthalpy [ $\Delta_{\text{sol}}H^\circ(\text{CO}_3\text{Ap})$ ] and “a,” “b,” and “c” factors as:

$$\Delta_f H^\circ(\text{apatite}) = -\Delta_{\text{sol}} H^\circ(\text{CO}_3\text{Ap}) - 5144.9 - 1113.74.(10 - a - b) - 1279.7.(6 - a - 2b - e) - 965.16.(a + 2b + e)$$

In which

$$(10 - a - b) = n\text{Ca}, (6 - a - 2b - e) = n\text{PO}_4, \text{ and } (a + 2b + e) = n\text{CO}_3$$

The mole numbers  $n\text{Ca}$ ,  $n\text{PO}_4$ , and  $n\text{CO}_3$  were determined experimentally from chemical analysis. **Table 3** gathers values of standard molar enthalpies of solution and formation for the group of samples.

As with the fluorine homologous compounds, the formation enthalpy increases with the amount of carbonate and thus the stability decreases.

It is assumed that only two kinds of carbonates are present in such compounds, consequently, among “a,” “b,” and “e” parameters, one has to be nil. Experimental results have been treated statistically in order to find which couple of parameters could be retained. Three relationships were derived from the general expression of the formation enthalpy and a mathematical model based on linear regression on two parameters was applied. The couple of parameters considered were (a,b), (a,e), and (b,e). A *F*-test analysis of variance was performed in order to get the significance level of values of the coefficients. The results show that “a” and “b” coefficients seem to be more significant in the expression of the formation enthalpy. So among I, II, and V mechanisms, the first two are the most probable ones. It seems that substitution of  $\text{CO}_3$  for  $\text{PO}_4$  in hydroxyapatites is more probably accompanied by the appearance of Ca an OH vacancies according to the two following mechanisms:

	$\Delta_{\text{sol}}H$ (kJ mol <sup>-1</sup> )	$\Delta_f H$ (kJ mol <sup>-1</sup> )
Ca <sub>9.83</sub> (PO <sub>4</sub> ) <sub>5.82</sub> (CO <sub>3</sub> ) <sub>0.28</sub> (OH) <sub>1.64</sub>	-387.76	-13133.3
Ca <sub>9.60</sub> (PO <sub>4</sub> ) <sub>5.55</sub> (CO <sub>3</sub> ) <sub>0.53</sub> (OH) <sub>1.49</sub>	-397.44	-12763.3
Ca <sub>9.35</sub> (PO <sub>4</sub> ) <sub>5.34</sub> (CO <sub>3</sub> ) <sub>0.67</sub> (OH) <sub>1.34</sub>	-396.05	-12352.6
Ca <sub>9.06</sub> (PO <sub>4</sub> ) <sub>4.95</sub> (CO <sub>3</sub> ) <sub>0.83</sub> (OH) <sub>1.61</sub>	-440.99	-11640.0
Ca <sub>8.93</sub> (PO <sub>4</sub> ) <sub>4.83</sub> (CO <sub>3</sub> ) <sub>1.06</sub> (OH) <sub>1.25</sub>	-421.71	-11583.0
Ca <sub>8.82</sub> (PO <sub>4</sub> ) <sub>4.74</sub> (CO <sub>3</sub> ) <sub>1.31</sub> (OH) <sub>0.80</sub>	-389.58	-11618.7
Ca <sub>8.86</sub> (PO <sub>4</sub> ) <sub>4.65</sub> (CO <sub>3</sub> ) <sub>1.37</sub> (OH) <sub>1.03</sub>	-420.20	-11575.4
Ca <sub>8.76</sub> (PO <sub>4</sub> ) <sub>4.59</sub> (CO <sub>3</sub> ) <sub>1.44</sub> (OH) <sub>0.87</sub>	-400.91	-11474.1
Ca <sub>8.68</sub> (PO <sub>4</sub> ) <sub>4.52</sub> (CO <sub>3</sub> ) <sub>1.58</sub> (OH) <sub>0.64</sub>	-387.48	-11443.9
Ca <sub>8.51</sub> (PO <sub>4</sub> ) <sub>4.41</sub> (CO <sub>3</sub> ) <sub>1.63</sub> (OH) <sub>0.53</sub>	-401.27	-11148.3

**Table 3.** Molar enthalpies of solution and formation for the B-type carbonate hydroxyapatites.

$\text{Ca}^{2+} + \text{PO}_4^{3-} \leftrightarrow \text{V}^{\text{Ca}} + \text{CO}_3^{2-} + \text{V}^{\text{OH}}$  and  $\text{Ca}^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{V}^{\text{Ca}} + 2\text{CO}_3^{2-}$  (and not mechanism V as reported erroneously in the conclusion and abstract of reference [21]).

## 7. Reactivity of B-carbonate fluorapatites toward the acid attack

### 7.1. Simple dissolution of Ca-CO<sub>3</sub>apatites

One of the criteria characterizing a phosphate ore is the speed of its reaction with acid solutions. This influences the reaction yield at a certain time and the self-heating rate of the reactional medium. The acid attack of synthetic and natural phosphates has been largely reported in the literature, but the quasitotality of works was performed by analysis of samples taken from the reactional medium. This way of doing does not give a true image of what is happening during the reaction. Microcalorimetry can overcome this drawback. However, this requires some preliminary experiments and signal treatment.

A C-80 SETARAM microcalorimeter has been adjusted in order to get calibration experiments in the same conditions as the chemical processes. This has been done by supplying the reversal cells of the device with electrical resistances that have been connected to a DC power supplier. When electrical energy is injected during a certain time in the reaction cell, this corresponds to an energy supplied in a “rectangular” shape but leads to a delayed and deformed recorded signal. This is because of the inertia of the various components of the device. A mathematical treatment allows to determine the time constants of the device and to get back the “rectangular” shape of the signal [21]. This “deconvolution” operation is particularly needed in studying fast phenomena. The time constants determined in the electrical calibration operation are then used for the chemical process in order to get a “deconvoluted” calculated curve which represent more accurately what happened inside the reaction cell when the reactants were mixed.

A series of B-type carbonate apatites having 1.53–5.94 wt% carbonate have been synthesized and characterized and then dissolved in 19w/w P<sub>2</sub>O<sub>5</sub> solution between 25 and 55°C using the C80- microcalorimeter. Dissolution of 10–60 mg of solid in 4.5 ml acid solution is a simple phenomenon without any resulting precipitate. The drawing of the energy released as a function of the solid amount led to the molar dissolution enthalpies as  $-201 \pm 4$ ,  $-208 \pm 5$ , and  $-205 \pm 5$  kJ mol<sup>-1</sup> for the 1.05, 3.05, and 5.94 wt% carbonate, respectively [22]. These values are lower than that corresponding to dissolution of carbonate-free fluorapatite in the same conditions ( $-171$  kJ mol<sup>-1</sup>). Introduction of B-carbonate in the lattice decreases the dissolution enthalpy and so confirms the decrease in stability.

As the dissolution is very fast, the deconvoluted curves were calculated taking into account the time constant values determined in calibration experiments. They were then analyzed according to Avrami model. This model links the reactant transformed fraction “*x*” to time through the following relationship:

$$-\ln(1 - x) = kt^n$$

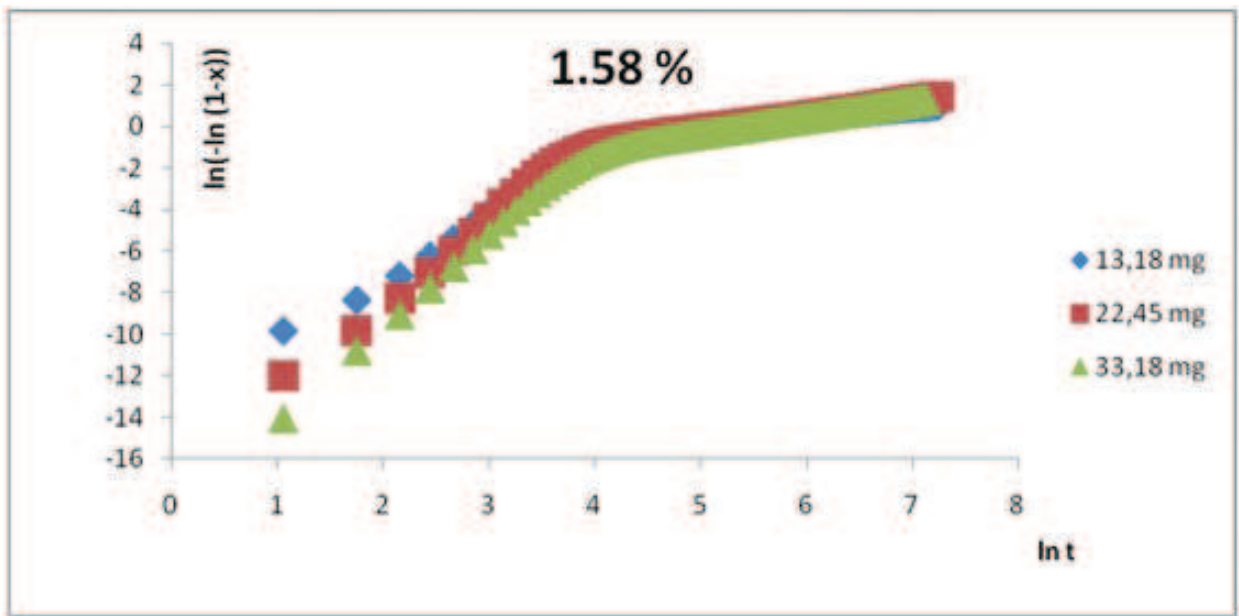
With *k* and *n* as the Avrami constants and “*x*” equals the ratio of the heat *q* released at time *t* over the overall heat *Q<sub>t</sub>* determined by integrating the whole peak. Originally, this model was

developed to interpret the kinetics of crystallization of a compound from its molten state. The procedure consists in drawing  $\ln[-\ln(1 - X)]$  as a function of  $\ln t$ . The existence of a slope change in the curve has been attributed to the appearance of a new phenomenon during a phase change. The model was then applied to the dissolution and precipitation process, such as dissolution of metals and oxides. Other studies also used this model for the interpretation of the dissolution and precipitation results of several products.

Applying this model to B-carbonate apatites reveals the existence of two processes, **Figure 9**, with a very short duration of the first one (33 seconds). It has been attributed to a surface phenomenon. The second one that lasts till 1200 seconds has been exploited to get a kinetic model of the acid attack. The results seem to be in agreement with a homogeneous model having an order of 2 with respect to the apatite. Activation energy values were deduced as  $15.8 \pm 1.4$ ,  $15.5 \pm 0.9$ , and  $8.5 \pm 0.5 \text{ kJ mol}^{-1}$  for the 1.58, 3.05, and 5.94 wt% carbonate, respectively [22]. These values are of the same order of magnitude as that determined for pure FAP below  $45^\circ\text{C}$  ( $16 \text{ kJ mol}^{-1}$ ) but drastically lower than that determined at higher temperature for the latter compound ( $101 \text{ kJ mol}^{-1}$ ) [23]. The lower value of the activation energy indicated that the reaction is rather controlled by a diffusion phenomenon.

7.2. Simple dissolution of Ca/Mg-CO<sub>3</sub>apatites

Different masses of Ca/Mg bearing B-type carbonate apatites having various amounts of carbonate have been dissolved in 3 wt% HCl solution at 25–55°C using the C-80 microcalorimeter. For low values of the solid/liquid ratio, no solid resulted and the recorded signals show the appearance of a process lasting until 2000 seconds. The drawing of the energy released at 25°C as a function of the solid mass allows to deduce the molar dissolution enthalpies from the slopes of the lines, **Table 4**.



**Figure 9.** Example of Avrami curves recorder for various masses of 1.58 w% CO<sub>3</sub> B-type F-apatite.

Apatite	$\Delta_{\text{sol}}H^\circ(\text{T}^\circ)$	Apatite	$\Delta_{\text{sol}}H^\circ(\text{T}^\circ)$
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	$-151.7 \pm 0.7$	$\text{Ca}_{8.60}\text{Mg}_{0.09}(\text{PO}_4)_5.16(\text{CO}_3)_{0.84}\text{F}_{1.83}$	$-209.7 \pm 1.1$
$\text{Ca}_{9.09}\text{Mg}_{0.91}(\text{PO}_4)_6\text{F}_2$	$-180.6 \pm 0.1$	$\text{Ca}_{8.36}\text{Mg}_{0.09}(\text{PO}_4)_{4.77}(\text{CO}_3)_{1.23}\text{F}_{1.75}$	$-222.7 \pm 0.3$
$\text{Ca}_{9.09}\text{Mg}_{0.09}(\text{PO}_4)_5.52(\text{CO}_3)_{0.48}\text{F}_{1.90}$	$-192.3 \pm 0.5$		

**Table 4.** Molar dissolution enthalpy in 3wt% HCl solution for Ca-FAP and Ca/Mg fluorapatites containing  $0.90 \pm 0.01$  Mg and various amounts of carbonate.

These values are higher than that obtained by dissolving the same products in the isoperibol calorimeter [24] and their difference increases with the carbonate amount. This is because the latter experiments were performed in a  $\text{CO}_2$  saturated solution, and so the solution is supposed to retain any further  $\text{CO}_2$ , while in the microcalorimeter the dissolution occurs in a hermetic cell and the  $\text{CO}_2$  released is partially dissolved in the resulting solution. This results in an exothermal increment in the dissolution energy that increases with the carbonate amount in the solid apatite. Appearance of such effect is in agreement with the diminution of solubility of gases in liquids when increasing temperature.

One can notice a decrease in the dissolution enthalpy when Mg is incorporated and a further decrease when introducing carbonates. Introduction of magnesium and carbonate decreases considerably the molar dissolution enthalpy.

The recorded signals were processed in order to get the corresponding deconvoluted (or thermogenesis) curves [25]. As previously, the Avrami curves drawn from the latter show at first very short phenomenon followed by a longer one. Treatment of the data reveals as previously, that the experimental results are in agreement with a homogeneous kinetic scheme with an order of 2 with respect to the apatite and an activation energy,  $E_a$ , decreasing from  $20.1 \pm 0.7$  to  $18.6 \pm 0.1$   $\text{kJ mol}^{-1}$  when only magnesium is introduced in the lattice.  $E_a$  decreases again to  $6.0 \pm 0.8$   $\text{kJ mol}^{-1}$  when the carbonate amount in the Mg-bearing apatites reaches 1.23 mol  $\text{CO}_3$  in the formula unit. The presence of magnesium and carbonate in B-carbonate F-apatites also seems to significantly decrease the activation energy of the acid attack and hence to increase considerably the velocity of the reaction.

However, the homogeneous kinetic model is far from the experimental reality since the reaction occurs between a solid and a liquid. Isoconversional model is more suitable for heterogeneous processes. According to this model, the converted fraction  $\alpha$  of a reactant is expressed as a function of time by the equation:

$$\frac{d\alpha}{dt} = kf(\alpha)$$

with  $k$  the rate constant and  $f(\alpha)$  a function associated to the mechanism. Integration of this equation leads to:

$$g(\alpha) = \int_0^\alpha \frac{dx}{f(x)} = kt$$

Considering the Arrhenius law,  $g(\alpha)$  can be expressed as:  $g(\alpha) = A \exp\left(-\frac{E_a}{RT}\right)t$

and so  $\ln(t) = \frac{E_a}{RT} + \ln\left(\frac{g(\alpha)}{A}\right)$

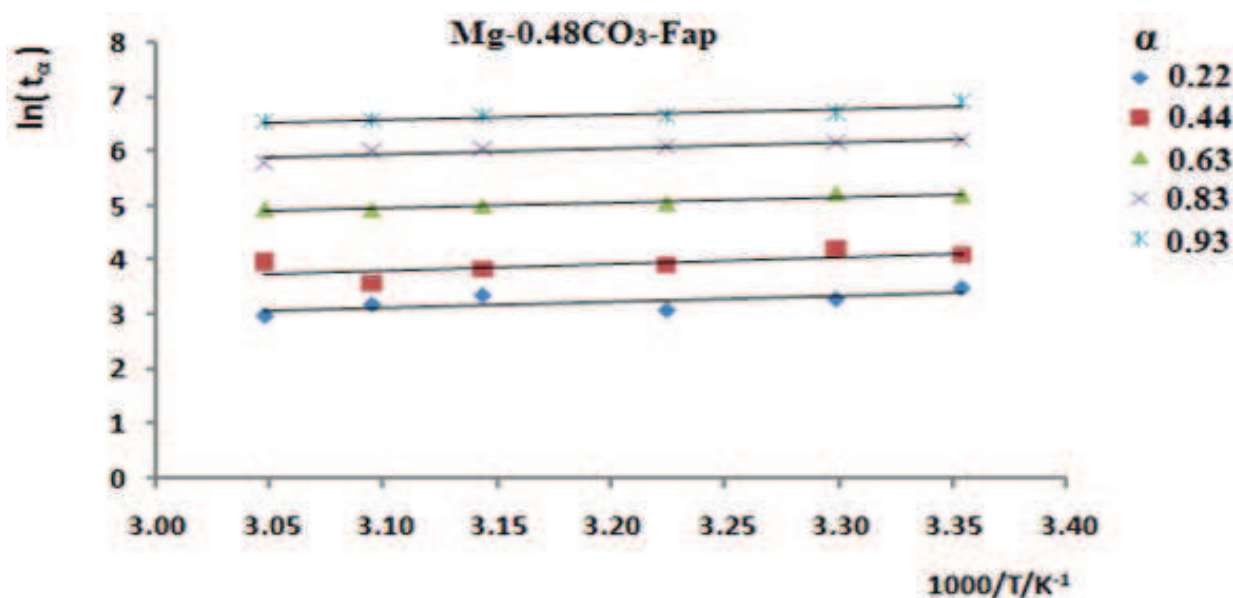
At a certain conversion rate,  $g(\alpha)/A$  is constant and so it is possible to determine the activation energy, whatever is the mechanism, by plotting  $\ln(t)$  versus  $1/T$ . Calculation was performed for  $\alpha$  in the range 0.06–0.98, and the activation energy was derived.

Examples of plots of  $\ln(t)$  versus  $1/T$  ( $25 \leq T \leq 55^\circ\text{C}$ ) for the Ca/Mg apatite containing 0.48  $\text{CO}_3$  are given in **Figure 10** (similar curves were obtained for all the apatites). The variation of the activation energy as a function of  $\alpha$  is represented in **Figure 11** for all the apatites with the corresponding errors calculated by considering the scatter of the points around the least square line drawn for each value of  $\alpha$  in **Figure 10** [25].

One can notice that the activation energy of any apatite is practically constant along all the process, suggesting a single-step reaction. Statistical calculations allowed to determine this quantity together with its error. The values are in the range  $21.1 \pm 0.3$ – $6.2 \pm 0.2 \text{ kJ mol}^{-1}$  for the series of compounds. It should be noticed that these values of  $E_a$  are in the range of their corresponding previous ones determined from the Arrhenius plots in the homogeneous kinetic model.

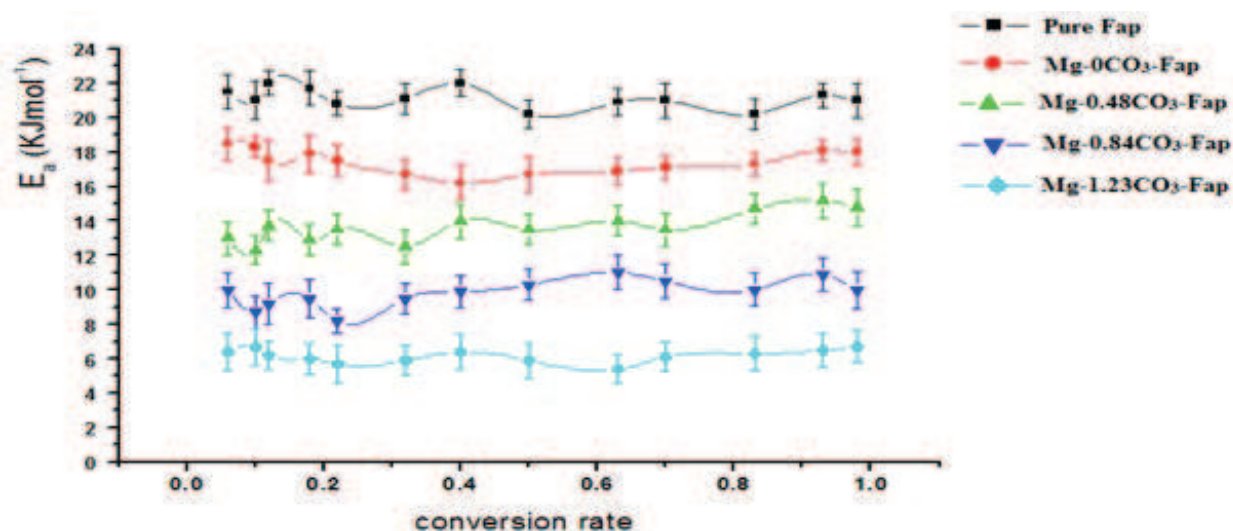
### 7.3. Dissolution of more amounts of Ca- $\text{CO}_3$ apatites

As with pure fluorapatite reported in Ref. [7], progressive dissolution of carbonated Ca-apatites in the same amount of a 19% w/w  $\text{P}_2\text{O}_5$  solution (4.5 ml) results in the occurrence of successive phenomena. This appears through the graph representing the energy released as a function of the solid amount. **Figure 12** shows an example corresponding to dissolution of the

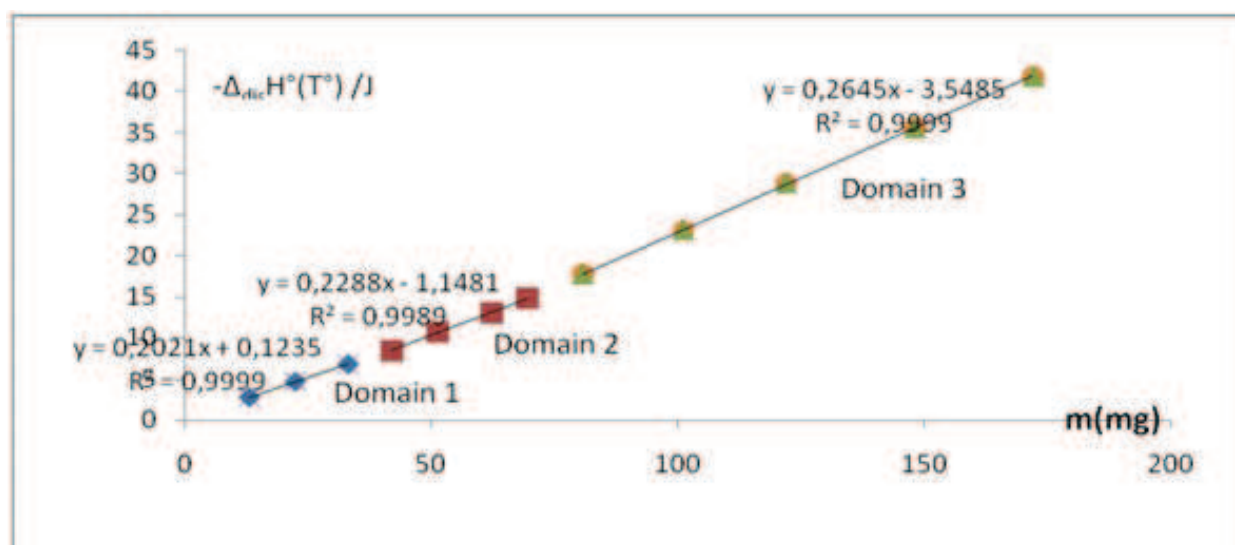


**Figure 10.**  $\ln(t)$  versus  $1/T$  ( $25 \leq T \leq 55^\circ\text{C}$ ) for the 0.48  $\text{CO}_3$  in Ca/Mg F-apatite.





**Figure 11.** Activation energies,  $E_a$ , versus the conversion rate,  $\alpha$ , for Ca/Mg F-apatites containing 0–1.23 carbonate in their lattice.



**Figure 12.** Heat energy at 25°C versus the mass of the 1.58 B-type carbonate F-apatite.

1.58 carbonate sample versus the solid mass. One can notice the presence of three domains, each one corresponding to a particular process.

Domain 1 corresponds to a simple dissolution, no precipitate appeared at the end of the process, while in domain 2 dissolution is followed by precipitation of  $\text{CaF}_2$  and in domain 3 precipitation of a mixture of the latter with MCPM (mono-calcium phosphate monohydrate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ). These precipitates were characterized by X-ray diffraction performed on the solids after reaction [26]. All the raw thermograms recorded in these domains indicated a unique phenomenon, while the thermogenesis curves in domains 2 and 3 show the successive appearance of two or three phenomena [26].

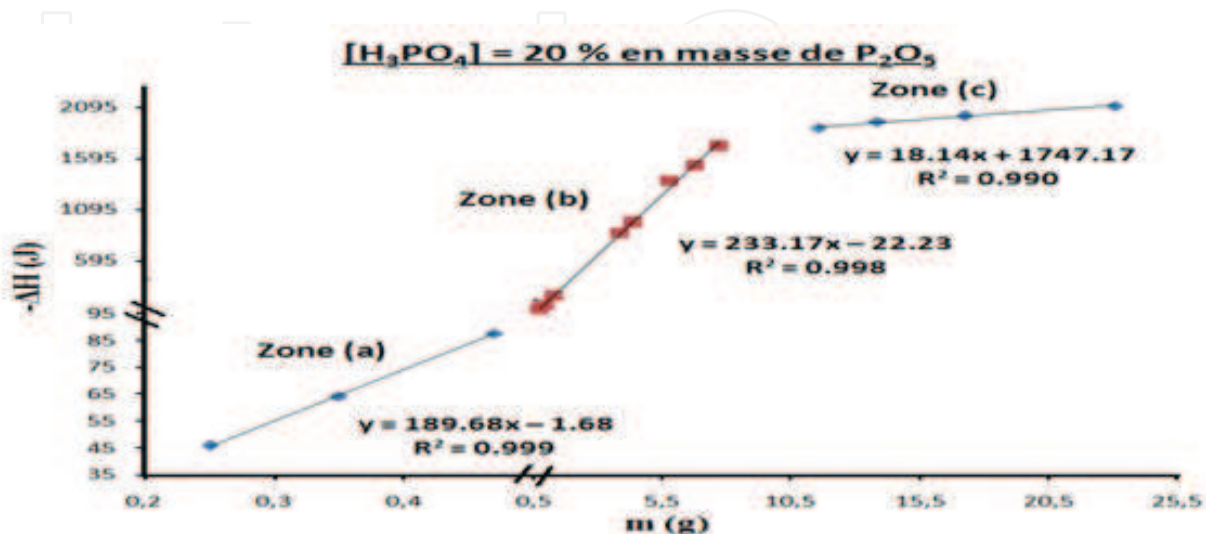


## 8. What about the phosphate ore?

It would be interesting to compare the behavior of the phosphate ore to that of these products. However, as the latter contains many compounds, dissolving a few dozens of milligrams is not representative of what is really happening. The differential reaction calorimeter (DRC) allows to overcome this difficulty. This device is composed of two symmetrical glass reactors of about half a liter maintained at the same temperature by a fluid circulating in a double envelop. Two axial agitators running at the same speed allow to disperse the solid in the liquid bulk. The former is initially introduced in a tubular sample holder and tightly separated from the liquid by a thin film blocking up the lower extremity of the tube. The recorded signal is a DC voltage resulting from the temperature difference between the two reactors that is detected by two thermocouples whose junctions are immersed in the liquids. The device has been calibrated and tested by experiments performed on key reactions [27].

A sample ore from Gafsa, Tunisia, has been previously chemically and structurally analyzed. It contains about 5.7 w%  $\text{CaCO}_3$  and 82.4 wt% of an apatite phase of formula:  $\text{Ca}_{9.25}\text{Na}_{0.52}\text{Mg}_{0.23}(\text{PO}_4)_{5.14}(\text{CO}_3)_{0.86}\text{F}_{2.34}$ . Various amounts (up to 40 g) of solid have been dissolved at 25–65°C in 100 g of an acidic solution having 20, 25, or 30 wt%  $\text{P}_2\text{O}_5$ . These compositions are of the same order of magnitude as that used in industrial manufacturing process of superphosphate fertilizer. As with B-type  $\text{CO}_3$  apatites at 25°C, attack of progressive amounts of solid by the same quantity of liquid show three domains each one corresponding to a particular phenomenon, **Figure 13**. Similar curves were obtained with 25 and 30 wt%  $\text{P}_2\text{O}_5$ .

The first domain corresponds to a simple dissolution with  $\Delta_{\text{diss}}H^\circ(T^\circ)$  in the range  $-189.7 \pm 2.1$  to  $-138.9 \pm 5.5 \text{ J g}^{-1}$  for 20, 25, and 30 wt%  $\text{P}_2\text{O}_5$ . The first value lies between that determined for the free Mg B-carbonate fluorapatites in 19 wt%  $\text{P}_2\text{O}_5$  (around  $-0.824 \times 212$  to  $-172.5 \text{ J g}^{-1}$  [17]) and that determined for Mg/ $\text{CaCO}_3$ -apatite containing 0.84  $\text{CO}_3$  in the lattice (around  $-0.824 \times 250$  to  $-206 \text{ J g}^{-1}$  [24]). The scatter cannot be explained by the presence of calcite in the ore, it could result from the presence of sodium in the apatite ore. Dissolution of Ca/Na carbonate F-apatites will help to get a better explanation. The second domain corresponds to dissolution then precipitation



**Figure 13.** Heat energy released at 25°C by dissolving m(g) of the Gafsa ore in 100g acid solution having 20wt%  $\text{P}_2\text{O}_5$ .

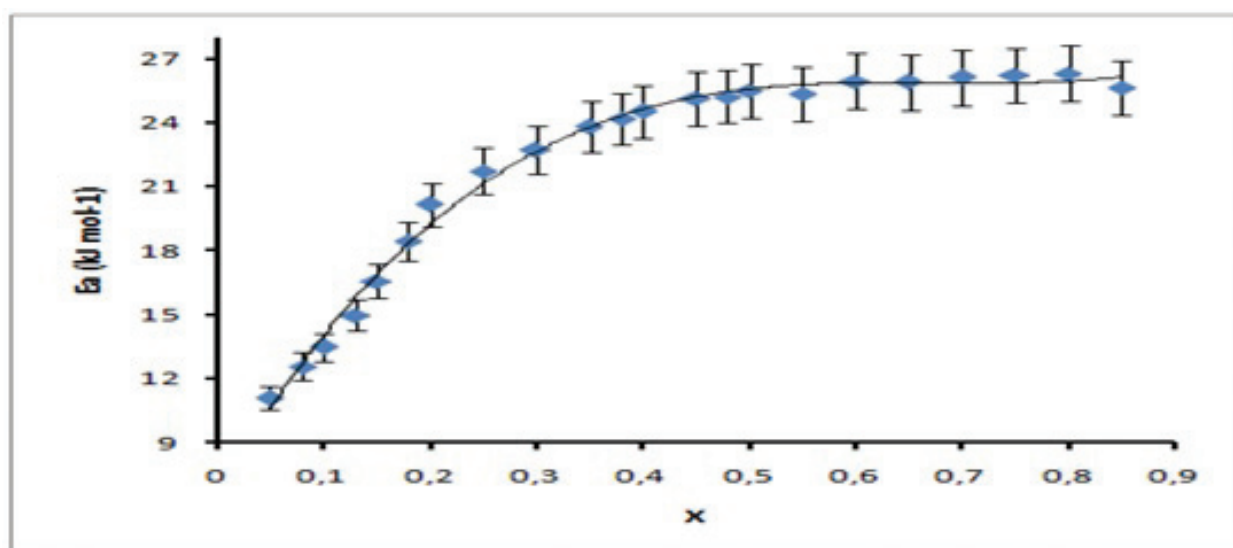
of MCPM,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  (and not  $\text{CaF}_2$  as with synthetic B-carbonates), and the third one to the appearance of a mixture of the latter with di-calcium phosphate dihydrate, DCPD,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  [28]. **Figure 13** also allows to determine the solubility of MCPM and DCPD in the acid solution. These quantities are calculated considering the intersection point of the straight lines and equal 0.47, 0.52 and 0.62 g for MCPM and 8.4, 11.8, and 10.3 g of solid per 100 g solvent for DCPD at 25°C in the three acid concentrations, respectively. At 65°C only domains 2 and 3 appeared, suggesting a very weak solubility of MCPM in these solutions at that temperature.

The kinetic model of the attack in domain 3 has established considering the thermogenesis curves. The Shrinking Core Model (SCM) seems to be in agreement with experimental results. According to this model, the reaction occurring between a solid and a liquid is controlled by one of the main following processes:

(1) diffusion of the liquid reactant through a liquid film surrounding the particle of the solid to the surface of the latter, (2) chemical reaction at the surface of the nonreacting solid, leading to the reaction product (or ash), and (3) diffusion of the resulting liquid through the ash back to the external surface of the solid. The following equations have been proposed for these processes [29]:  $X = kt$ ,  $[1 - (1 - X)^{1/3}] = kt$  and  $[1 - 3(1 - X)^{2/3} + 2(1 - X)] = kt$ , where  $X$  is the conversion fraction of solid,  $k$  is the kinetic constant, and  $t$  is the time.

Calculation performed on the thermogenesis curves lead to conclude that the experiment results are in agreement with the third process. An activation energy value has been deduced as  $25.4 \pm 1.8 \text{ kJ mol}^{-1}$ , and so the acid attack seems to be controlled by the ash diffusion phenomenon.

However, this model describes globally the process and does not take into account the evolution of the reaction scheme resulting from the modification of the grain surface during the reaction. The isoconversional model allows to take into account this phenomenon. Applying this model to the process occurring in domain 3 led to straight lines representing  $\ln(t)$  as functions of  $1/T$  for various values of the conversion rate, as in **Figure 10**. The deduced activation energy  $E_a$  values allow to draw the latter quantity as a function of  $X$ , **Figure 14**.



**Figure 14.** Activation energy ( $E_a$ ) as a function of the conversion rate ( $x$ ) according to the isoconversional model.

Value of  $E_a$  determined in the SCM model ( $25.4 \pm 1.8 \text{ kJ mol}^{-1}$ ) belongs to the interval values corresponding to the isoconversional model, which lies in the range  $11.1\text{--}26.3 \text{ kJ mol}^{-1}$  and the shape of the curve indicates that the process does not occur in only one step. It could be a successive or consecutive reaction process [30].

In conclusion, thermodynamic determinations allow to point out the influence of the various components on the stability and reactivity of the apatites. The results show that introduction of carbonate along the channel contributes to increase the stability of F-apatites, while in B-type fluor- and hydroxyl-apatites, the carbonate ions contribute to decrease the stability. It is also for the substitution of calcium by magnesium. B- $\text{CO}_3$  and Mg-substitutions increase the reactivity of synthetic F-apatites toward the acid attack that seems to be a one step process, while the acid attack of natural phosphate is more complicated.

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